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Enabling liquid vapor analysis using synchrotron VUV single photon ionization mass spectrometry with a microfluidic interface

R. Komorek,[1,b)] B. Xu,[2] J. Yao,[1,b)] U. Ablikim,[2] T. P. Troy,[2] O. Kostko,[2] M. Ahmed,[2] and X.Y. Yu,[1, a),b)]

[1]*Atmospheric Sciences and Global Change Division, PNNL, Richland, WA. 99354, United States*

[2]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA. 94720, United States*

Vacuum ultraviolet (VUV) single photon ionization mass spectrometry (SPI-MS) is a vacuum-based technique typically used for analysis of gas phase and solid samples, but not for liquids, due to the challenge in introducing volatile liquids in vacuum. Here we present the first demonstration of *in situ* liquid analysis by integrating the System for Analysis at the Liquid Vacuum Interface (SALVI) microfluidic reactor into VUV SPI-MS. Four representative volatile organic compound (VOC) solutions were used to illustrate feasibility of liquid analysis. Our results show accurate mass identification of the VOC molecules and reliable determination of appearance energy (AE) that is consistent with ionization energy (IE) for gaseous species in literature as reported. This work validates that the vacuum-compatible SALVI microfluidic interface can be utilized at the synchrotron beamline and enable *in situ* study of gas-phase molecules evaporating off the surface of a liquid, which holds importance in the study of condensed matter chemistry.

Key words: SALVI, VOCs, appearance energy, ionization energy, liquid, VUV single photon ionization mass spectrometry

I. INTRODUCTION

Single photon ionization with VUV photons is an efficient and "soft" method of ionizing fragile molecules, whereby tunable radiation provides precise threshold ionization imparting little excess internal energy into the molecular ion.[1-6] This greatly reduces the extensive fragmentation usually observed with multiphoton or electron impact ionization techniques.[7] Furthermore, tunable VUV ionization has been shown to be a selective, yet universal technique in elucidating molecule-specific information since it can distinguish isomers via ionization energy (IE) and absorption cross-sections following rules that are quantifiable. This has allowed its applications in biology,[8, 9] combustion chemistry,[10] and atmospheric chemistry.[3] However, liquids have not been often used thus far in single photon ionization mass spectrometry (SPI-MS) applications, because some of them are highly volatile and difficult to retain in vacuum; for a successful VUV SPI-MS measurement, the main chamber vacuum

b) mail: xiaoyingyu@pnnl.org

b) This research was performed while R. Komorek, J. Yao, and X.Y. Yu were at LBNL

is preferably maintained at 10^{-7} Torr.[11, 12] Thus, SPI-MS as a vacuum technique has been traditionally restricted to measurements of solid and gas phase samples or liquids with very low volatility such as some ionic liquids. Liquids, particularly those with low vapor pressure, however have been delivered into the gas phase in the form of aerosols,[13-15] and via laser and thermal desorption from substrates for cholesterol[16] and for pyruvic acid.[17] However, the study of liquids, particularly reactive chemistry is important, as many chemical processes take place at the gas-liquid or air-liquid interface in various applications, which have unique kinetics and thermodynamics.[18, 19] The traditional approach of aerosols or laser desorption does not allow direct sampling from the liquid phase, where reactions occur in the gas-phase when the VUV photoionization sampling takes place. We present a solution to the challenge of liquid investigation in VUV SPI-MS by using a portable and vacuum compatible microfluidic reactor known as System for Analysis at the Liquid Vacuum Interface (SALVI).[11, 20, 21]

SALVI was invented initially to enable liquid analysis in time-of-flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy (SEM), both of which are vacuum-based techniques.[11, 21, 22] SALVI has been successfully applied to study a variety of liquids using SIMS[23-28] and SEM[29-31] under high vacuum conditions, generally with main chamber vacuum on the order of 10^{-6} to 10^{-7} Torr, and is compatible with *in situ* studies of complex liquids, such as bacterial biofilms, single cells, complex liquid mixtures, and switchable ionic liquids.[26, 28, 32] The SALVI device consists of a polydimethylsiloxane (PDMS) microfluidic microchannel for providing liquid under vacuum. When placed in the SPI-MS vacuum chamber, the liquid evaporates from the two micrometer (2 μm) apertures on the silicon nitride (SiN) membrane with liquid underneath.[11, 22]

In this communication, we present the combination of SALVI and SPI-MS to enable the *in situ* study of molecules evaporated from solution. Four volatile organic compounds (VOCs) of interest in atmospheric chemistry: phenol, toluene, pyruvic acid, and oxalic acid, were chosen to illustrate the effectiveness of this new approach. Each VOC has been studied in the gas phase and is known to participate in air-liquid reactive uptake followed by photochemistry to form secondary organic aerosols (SOAs) in the atmosphere.[33-36] The demonstration of reliable gaseous analysis using SPI-MS over the liquid surface sets the technical foundation for future scientific investigation. Molecular identification based on the mass spectra is determined and Appearance Energy (AE) values of each compound are compared to known IE for species identification and measurement accuracy. Key results show accurate determination of AE and IE values in liquid when compared to those in the gas phase, demonstrating the novel SPI-MS capability for *in situ* study of highly volatile liquids in vacuum and presenting possibilities to use the pump-and-probe approach for future study of the dynamic photochemistry at the air-liquid interface.

II. EXPERIMENTAL

A. SALVI fabrication

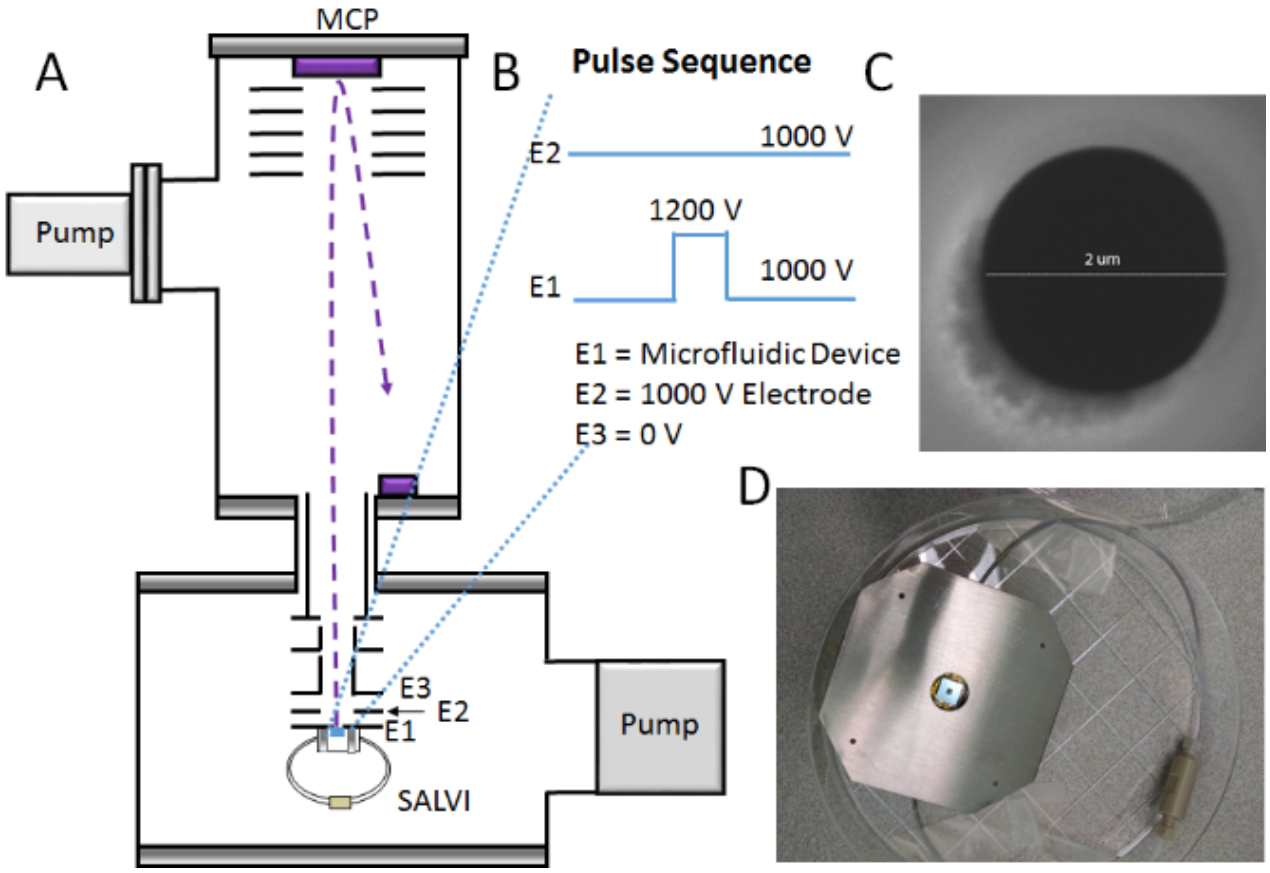

FIG. 1. A schematic showing the SALVI integration to the VUV SPI-MS. Insert A) gives the electrode scheme in the ion optics of ReToF MS with the attached SALVI device, B) provides voltages and the pulse sequence of ReToF MS ion optics, C) a secondary electron image showing the 2 µm diameter hole on the SiN membrane, and D) a photo showing SALVI adapted to the ion optics plate. The SALVI device is attached to the bottom electrode in A. The schematic diagram in A was adapted from Kaiser R.I. *et al*. 2010 and Góbi, S. *et al.* 2018.[3-6]

To fabricate the SALVI microfluidic device, soft lithography was applied to make a 200 µm wide by 300 µm deep channel on a silicon wafer as the mold. PDMS was filled in the mold to form the block with the channel after it was hardened. Two pieces of 1.59 mm polytetrafluoroethylene tubing (I.D. 0.58 mm) were interfaced to the PDMS block and attached to two pieces of polyetheretherketon (PEEK) tubing (I.D. 0.51 mm) that were connected to the microchannel. A 100 nm thick SiN membrane window supported on a silicon frame (frame size 7.5×7.5 mm^2, window size 1.5×1.5 mm^2, Norcada) was irreversibly bonded to the PDMS block by oxygen plasma treatment.[11, 22] Two holes of 2 µm in diameter with 100 µm apart were pre-milled using the Focused Ion Beam of a FEI Quanta 3D FEG SEM (FIB/SEM) in the center of the microchannel on the SiN membrane. The secondary electron image (**Fig. 1C**) of the hole was taken at 100, 000 magnification and 1024 × 884 resolution, using ~47.3 pA electron beam current and 5 keV accelerating voltage with a scan rate of 20 µs. The working distance was set to ~ 7 mm when obtaining this image. The SALVI devices were sputter coated with a thin layer of gold (Au) of

approximately 50 nm to make them conductive and integrable as one of the electrodes in the ion optics module of the SPI-MS (see **Fig. 1**). Prior to experiment, SALVI devices were degassed in a vacuum oven (VWR, product number 10752-398) at 50 °C overnight to reduce the potential interference from the PDMS due to its permeability.[11]

B. SALVI integration to VUV SPI-MS

After degassing in a vacuum oven overnight, the SALVI device was filled with solution and fixed to the bottom electrode plate (E1) (seen in **Figures 1A-D**) of the Reflectron (Re) ToF-MS. The SiN membrane was aligned with a through-hole with a diameter of 2 μm in the center of the bottom electrode plate (E1). This ReToF-MS was coupled to a three-meter VUV monochromator at the 9.0.2 Chemical Dynamics Beamline at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory. The height of the mass spectrometer was optimized to ensure that the distance between the SiN membrane and the VUV light was about 5 mm. The molecules evaporated from the 2 μm holes were ionized by VUV light and the ions were accelerated and detected by the mass spectrometer. The number of molecules evaporated from the aperture is estimated to be approximately in the order of 10^8 per cm^2 per second.[2] ToF mass spectra were measured for photon energies in the range between 8.0 and 12.5 eV at 0.1 eV increments using a LabView program. Slightly different microchannel plate (MCP) voltage was used for each VOC to obtain optimized signals. The mass calibrations are performed introducing well studied samples in the mass spectrometer chamber, such as water, oxygen, nitrogen or rare gases. The tunable photon energy from a synchrotron allows efficient ionization of all gas-phase samples and their distinction based on different IEs. The photoionization efficiency (PIE) curves were obtained by integrating over the mass peaks at each photon energy and normalizing with respect to photon flux measured by a silicon photodiode.[3] Data were plotted using OriginPro®.

C. Sample preparation

Phenol (99%), toluene (98%), pyruvic acid (99%), and oxalic acid (99%), all of ACS grade, were acquired from Sigma Aldrich and used as is. Sample preparation was conducted by dissolving solutes in deionized water (DI). Deuterated water (D_2O) oxide (Sigma Aldrich 99.9% grade) was added in the mixture as an internal standard. After full dissolution, pH levels of each solution were measured (Mettler Toledo model 51302803). The oxalic acid solution was prepared to be 0.5 M with a pH of 0.71. Pyruvic acid was prepared at a 0.25 M concentration with a pH of 1.30. The phenol solution was at 0.25 M with a pH of 5.6. Toluene was prepared at a concentration of 0.25 M with a pH of 6.4. Liquid samples were injected into the SALVI loop by using PEEK fittings and a luer lock connector. Static samples were used for the validation experiments here, although flowing liquid is possible by making connections via a feed-through in the chamber.[37]

III. RESULTS AND DISCUSSION

A. MASS SPECTRAL ANALYSIS

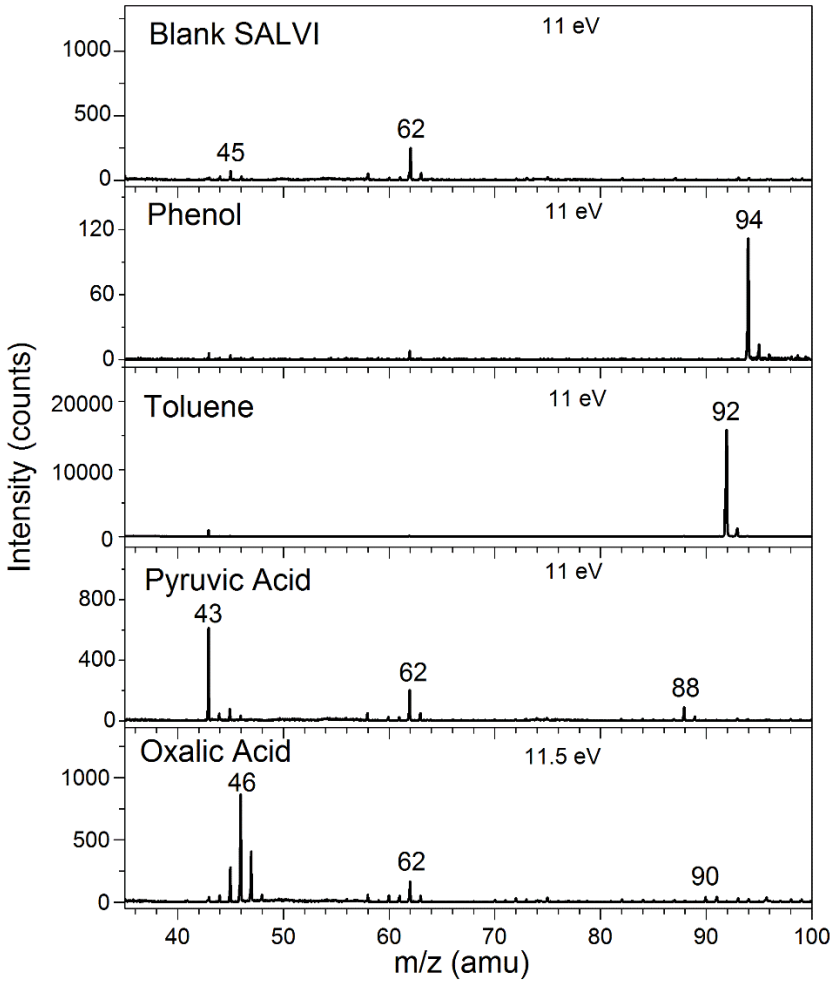

FIG. 2. SPI-MS spectra in the positive mode, with PDMS background subtracted to show observations of molecular ions in each of five samples including the blank SALVI control, phenol, toluene, pyruvic acid, and oxalic acid.

The ToF mass spectra of the four selected VOCs and a blank SALVI device control spectrum measured at 11 eV or 11.5 eV photon energy are shown in **Figure 2**. While water was used as a solvent in this study, it should be noted that other solvents may be used to successfully study liquid in vacuum systems.[28] The blank SALVI device with no liquid serves to show expected background peaks that may come from PDMS interference or residues from previous experiments in the main chamber.[38, 39] As expected, there was a prominent peak at m/z 94 in the phenol (C_6H_6O, m/z 94.11) mass spectrum and at m/z 92 for the toluene (C_7H_8, m/z 92.14) sample, confirming the presence of gas-phase phenol and toluene after evaporation as detected by SPI-MS. There were very low intensity peaks at the expected values for the remaining two VOCs when compared to the first two, with a small peak at m/z 88 for pyruvic acid ($C_3H_4O_3$, m/z 88.06) and at m/z 90 for oxalic acid ($C_2H_2O_4$, m/z 90.03). The smaller intensity of these two molecules are due to their tendency to fragment induced by ionization, which

was also observed in previous studies performed using electron impact ionization.[40, 41] The peak at m/z 43 is the main fragment of pyruvic acid, while m/z 45, 46, and 47 are fragments of oxalic acid. Bhattacharya et al. performed thermal desorption of pyruvic acid in a molecular beam followed by VUV and IR-VUV photoionization at 10.5 eV photon energy.[17] They obtained a parent ion signal at m/z 88 followed by a fragment at m/z 43 corresponding to H_3CCO^+ which they attributed to direct C_α-$C_{carboxylic}$ bond dissociation. They discussed at length, supported by IR spectroscopy and theoretical calculations, as to the nature of this fragmentation that was dependent on the specific conformation of the alpha substitution. We have also observed similar fragmentation behavior in alcohols (glycerol)[42] and sugars (deoxyribose)[43] where even single photon ionization at threshold can lead to extensive fragmentation which is explained by theoretically following the dynamics of their respective ionic potential energy surfaces.

B. AE Determination

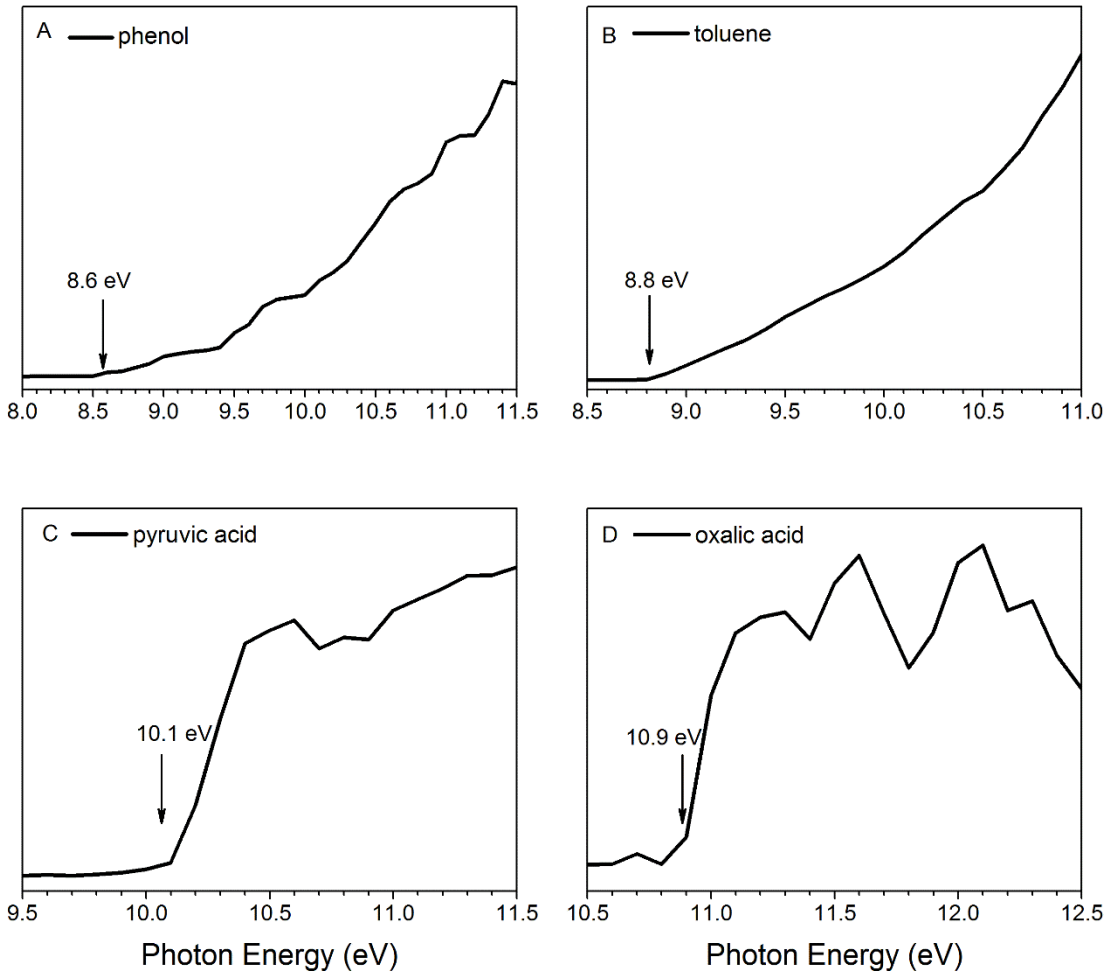

FIG. 3. PIE curves for the four VOCs dissolved in DI water: A) phenol, B) toluene, C) pyruvic acid, and D) oxalic acid. Arrows point to the AE value for each VOC.

Photoionization efficiency curves derived from the experimental data are presented in **Figure 3**. AE values were determined from the PIE spectra and the obtained AE values are summarized in **Table 1**. When looking at the PIE curves in **Figure 3**, the empirically determined AE values are found as the first photon energy at which the line deviates from zero intensity when increasing the photon energy. The AE value corresponds to the minimal amount of energy needed to remove the valence electron from initially neutral molecule to form a cation.[44, 45] In absence of molecular fragmentation, the AE is the adiabatic ionization energy (aIE) and can be compared to the literature findings of aIE.

The AE value determined for **phenol** was found to be 8.6 ± 0.1 eV, which was close to the recently reported aIE of 8.506 ± 0.001 eV that was measured using UV light with two color multiphoton ionization.[46] The most recent study used pump-probe photoionization in a ToF mass spectrometer, and reported an IE of 8.508 eV ± 0.001 eV, which was commensurate with the IE obtained in this work.[47] The AE value determined for **toluene** using the liquid phase SALVI approach was 8.8 ± 0.1 eV, which is well within 0.1 eV of the NIST recommended value of 8.8 eV.[41] The aIE value determined previously is 8.82 ± 0.01 eV, which is within 0.1 eV of the value determined using our in situ liquid analysis.[48] The vertical IE (vIE) value determined using photoelectron spectroscopy for **pyruvic acid** was 10.42 eV.[49] The onset of the published photoelectron spectrum roughly corresponding to the aIE was observed at 10.0 eV.[49] Our value of 10.1 ± 0.1 eV is in agreement with that value. Lastly, **oxalic acid** has vIE of 11.2 eV, which was determined in each of three studies utilizing photoelectron spectroscopy.[50-52] The onset of the photoelectron spectrum of m/z 90 was observed at 10.9 ± 0.1 eV. Our values are consistent with these previous measurements. **Table 1** shows a summary and comparison of the AE values determined in this work with NIST recommended values.

TABLE I. Comparison of AE values from SALVI SPI-MS experiment with NIST IE values.

Chemical Compound	AE (eV)	IE (eV)	Notes	Reference
Phenol	8.6 ± 0.1	8.506 ± 0.001	aIE	Fuke, Yoshiuchi*, et al*., 1984[46]
Toluene	8.8 ± 0.1	8.82 ± 0.01	aIE	Traeger and McLoughlin, 1978[48]
Pyruvic acid	10.1 ± 0.1	10.42	vIE	McGlynn and Meeks, 1975[49]
Oxalic acid	10.9 ± 0.1	11.20	vIE	McGlynn and Meeks, 1976[50]

Overall, AE results obtained from liquid vapor analysis using SALVI coupled to VUV SPI-MS are in good agreement with IE values reported before. Consistent molecular identification to NIST and other literature sources suggests that a liquid sample can be used for accurate *in situ* analysis of gas phase evaporation when integrating SALVI and synchrotron VUV SPI-MS. Furthermore, contrary to photoelectron spectroscopy, which provides ionization energies only without mass identification, a mass spectrometry approach described here provides a window into complex mixtures that will occur under reactive conditions. We believe, our approach of sampling the gas phase directly from a solution will open up the field of SPI-MS to a series of new opportunities in liquid phase electro- and photo-chemistry. Recently, tightly focused light from a VUV laser was used to image

molecules directly ablated from biological material and it was demonstrated that this method offered lower levels of fragmentation and higher sensitivity compared to other forms of ionization such as MALDI and SIMS.[53] Our group has also demonstrated that tightly focused laser light coupled with VUV post ionization also provided greater sensitivity and higher lateral resolution (5 μm) when probing organic and biological molecules.[54] Since VUV light below 11.0 eV can be easily focused with MgF_2 lenses, it is reasonable to believe, that tightly focused VUV light can be directly impinged on the SALVI device to probe the liquid surface. In addition, we believe coupling tightly focused VUV and X-ray light directly on the SALVI device would be beneficial in generating photoelectrons, and coupling these with velocity map imaging optics (as demonstrated recently on liquid aerosols)[55] should provide a new way to probe liquids.

V. SUMMARY AND CONCLUSIONS

A vacuum compatible microfluidic interface SALVI is coupled with a synchrotron VUV SPI-MS to obtain the IEs of several VOCs of importance in atmospheric chemistry. Four different VOCs were investigated and the results were compared with literature values to determine the validity of using microfluidics to introduce liquid and study properties of the liquid phase using synchrotron capabilities. The mass spectra provided accurate representations of each of the VOCs at their respective m/z values, although the pyruvic and oxalic acids had lower intensities in their respective mass spectra due to the lower vapor pressure of these compounds. The PIE curves were obtained. The empirical AE values obtained from the PIE curves are close to the IE values recommended by NIST. Our results suggest that the in situ liquid approach provide equally viable results as those in the gas phase. More importantly, this study has effectively proven the practicality of conducting gas analysis over liquids using SALVI integrated with the vacuum-based VUV SPI-MS at the ALS facility. This new approach opens up a leading-edge avenue to study challenging liquids and complex systems involving liquid using the synchrotron, for instance in dynamic study of photochemical multiphase reactions of VOCs and electrochemistry of volatile organic electrolyte in the future.

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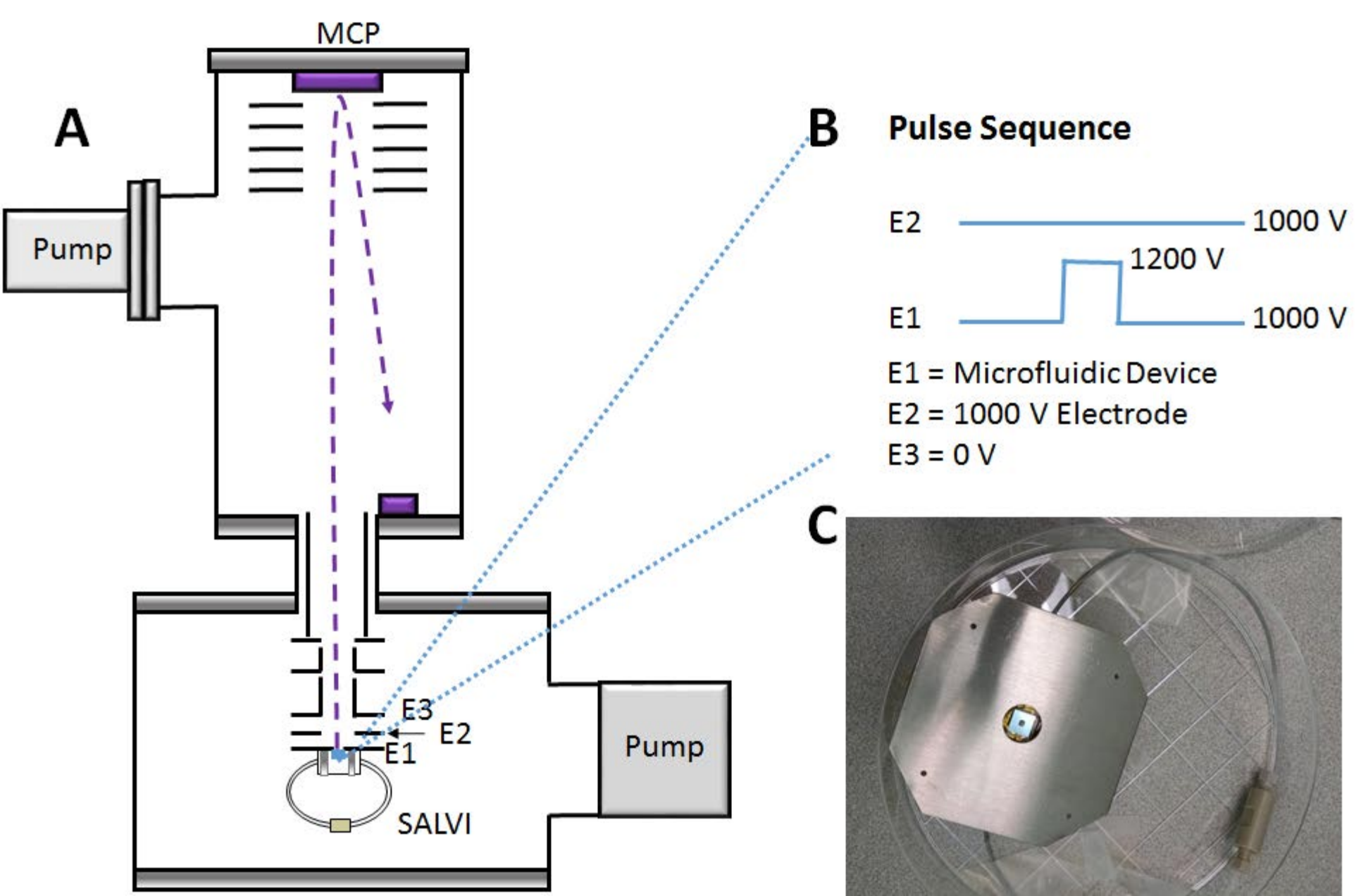
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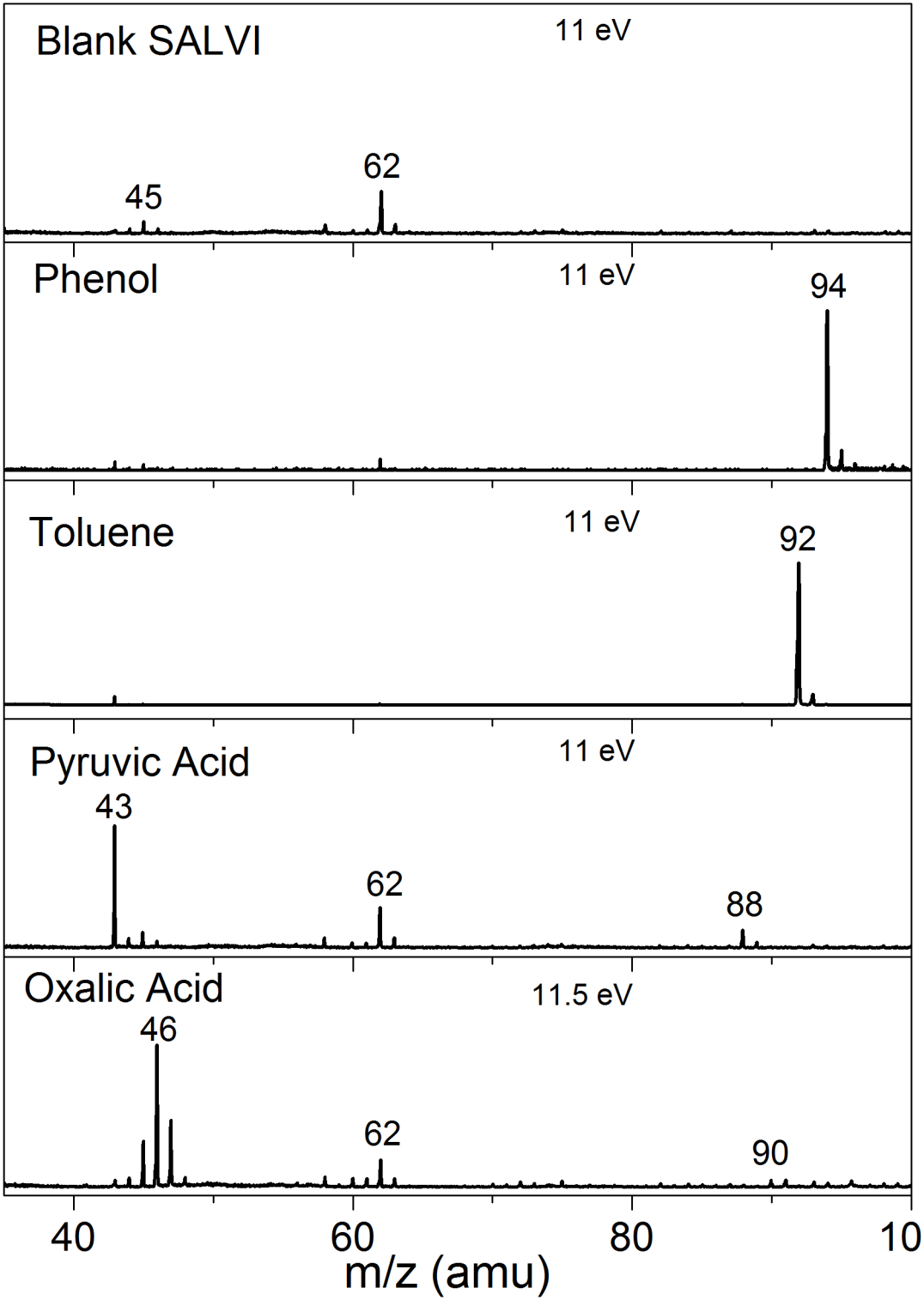
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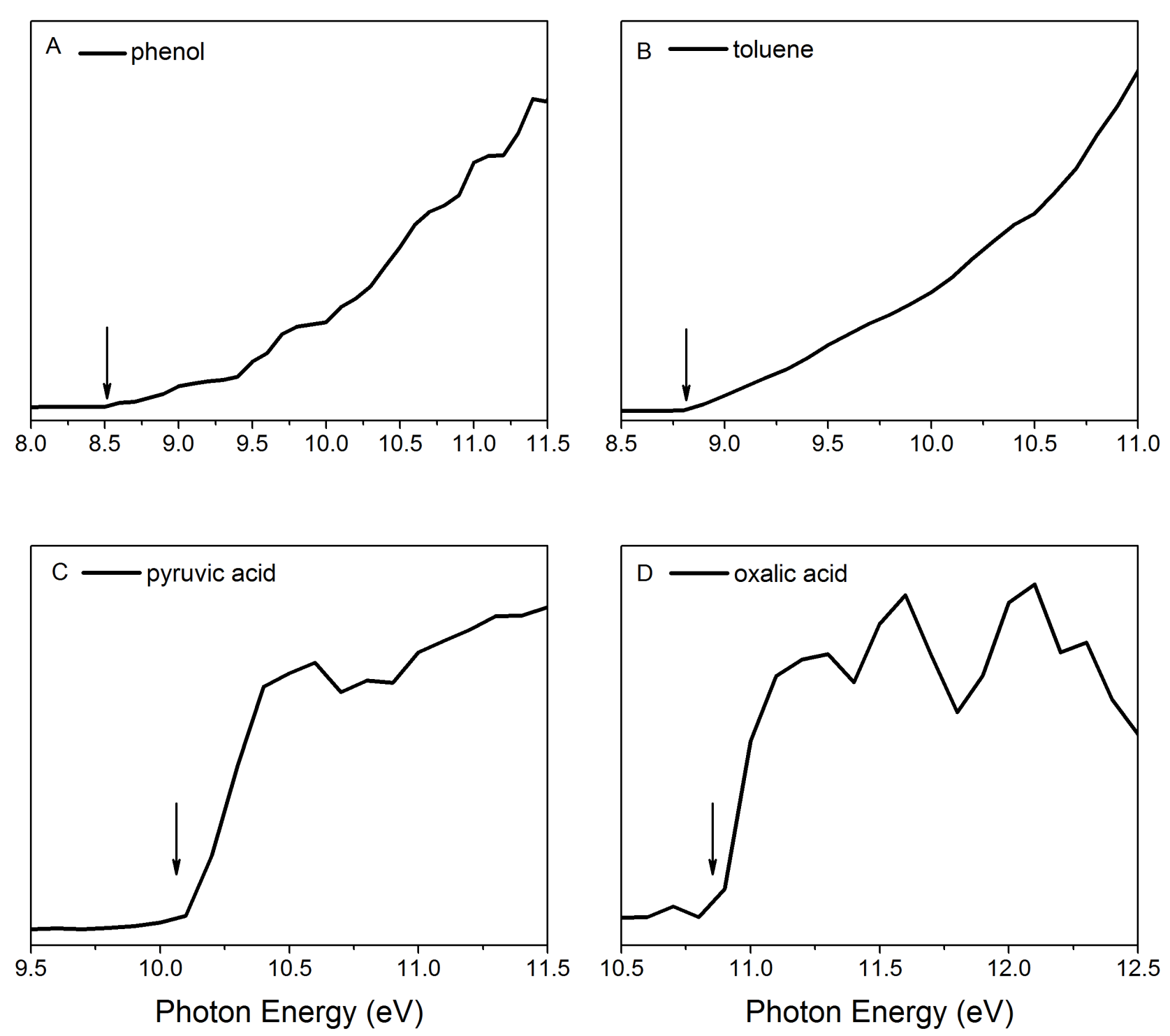
80
100
m/z (amu)


A
phenol
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
B
toluene
8.5
9.0
9.5
10.0
10.5
11.0
C
pyruvic acid
9.5
10.0
10.5
11.0
11.5
Photon Energy (eV)
D
oxalic acid
10.5
11.0
11.5
12.0
12.5
Photon Energy (eV)